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SPECTRAL STRUCTURE OF THE PHOSPHORESCENCE OF CERTAIN SULPHIDES.[1]

DISCUSSING MEASUREMENTS BY DRS. H. E. HOWE, H. L. HOWES AND PERCY HODGE.

BY EDWARD L. NICHOLS.

(Read April 13, 1917.)

Ph. Lenard, to whom we owe extended studies of the class of highly phosphorescent substances known as the Lenard and Klatt[2] sulphides, describes[3] the spectrum of the emitted light as consisting of a single broad band in the visible spectrum. This band which appears single, in most cases, as viewed with the spectroscope does not however conform to the recognized criteria. The marked difference between the color of fluorescence and that of phosphorescence and the changes of color during decay, suggest overlapping bands. E. Becquerel[4] in 1861 showed in his pioneer work on phosphorescence, that the color of the emitted light varies with the wavelength of the exciting light. His observations apply, it is true, to sulphides of barium, calcium and strontium not identical in make-up with the sulphides of Lenard and Klatt but obviously belonging to the same class. In a recent paper[5] the present writer gave more direct evidence of the existence of more than one band in the spectra of these substances. In that investigation which dealt primarily with the phenomena of color as seen in the phosphorescence, it was shown that with the aid of a special form of phosphoroscope[6] which permitted of the observation of phosphorescence during the first few thousandths of a second after the cessation of excitation as well as later, various marked changes of color during decay not previously noted could be detected. These changes were readily explained by the assumption of overlapping bands, one of which decays with great rapidity and vanishes in a few thousandths of a second, while the other persists. The actual existence of these two components was readily verified:

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[1] An investigation carried out in part with apparatus purchased by aid of a grant from the Carnegie Institution of Washington.

[2] Lenard and Klatt, *Ann. der Physik.*, XV., p. 225, 1804.

[3] Lenard, *Ann. der Physik.*, XXXI., p. 641, 1910.

[4] E. Becquerel, *La Lumiere,* Vol. I., 1861.

[5] Nichols, *Proc. Am. Philos. Soc.*, 55, p. 494, 1916.

[6] Nichols, *Proc. Nat. Acad. Sc.*, II., p. 328, 1916; also Nichols and Howes, *Science,* N. S., XLIII., p. 937, 1916.

1. By observing the spectrum of the light as viewed through the openings of the phosphoroscope. One end of the band could be seen to collapse immediately after the cessation of excitation, *i. e.*, the end towards the violet in the case of the luminous barium sulphides and the end towards the red when the sulphides of calcium or strontium were under observation.

2. By exciting the substance at the temperature of liquid air. Under these conditions the persistent band was completely destroyed leaving only the band of short duration visible in the phosphoroscope; with consequent change of color.

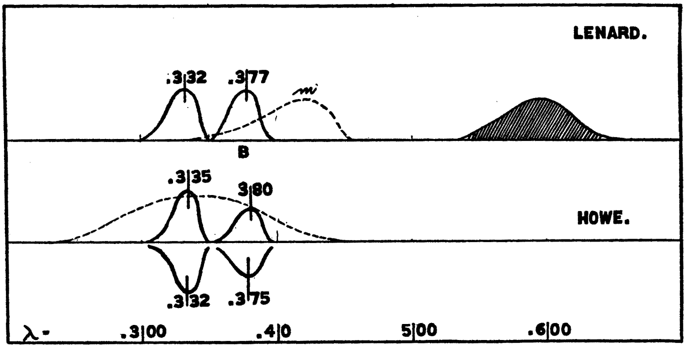

Fig. 1.

It should be noted in this connection that in their original paper[7] Lenard and Klatt depicted these spectra as complex, while in his latest paper, already cited, Lenard prefers to regard them as single. This later view may be most briefly and conveniently indicated by the upper part of Fig. 1, which is a typical diagram reproduced from Lenard's plate. Here the shaded area represents the location of the band of emission, indicated as a single broad band and the two enclosed areas *BB* in the ultra-violet show the regions capable of exciting phosphorescence. These two crests or so-called bands of excitation (Erregungsbände) have fixed positions as to wave-length, for each sulphide.

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[7] Lenard and Klatt, *Ann. der Physik,* (4), XV., p. 225, 1904.

SIGNIFICANCE OF THE BANDS OF EXCITATION.

It seemed to the writer probable that these regions of maximum excitation, the positions and appearance of which had long since been beautifully depicted by Becquerel in the work already cited, were due to the presence of absorption bands. Dr. H. E. Howe who was employed during the past summer in the study of the ultra-violet absorption spectra of certain fluorescent solutions, was kind enough to test this hypothesis. Following the method developed by Stokes and by Becquerel and subsequently used by Lenard and Klatt, the phosphorescent substance was exposed to the dispersed rays of a large quartz spectrograph. The source of light was the powerful submerged aluminum spark described by *Henri*[8] and subsequently employed by Howe[9] in his study of absorption spectra. This affords a continuous spectrum of great intensity extending to about $.2\,\mu$. A considerable portion of the ultra-violet spectrum was found capable of exciting fluorescence. In the case of a barium sulphide with lead with a flux of sodium sulphate this broad band of excitation, corresponding to Lenard's "Momentanband," extended from $.42\,\mu$ to about $.23\,\mu$. It is indicated by the dotted line in the lower diagram in Fig. 1. Upon this were gradually developed two narrow crests or maxima which glowed for sometime after the close of excitation, the "Dauerbände" of Lenard. The wave-lengths of these crests were estimated as $.380\,\mu$ and $.335\,\mu$, Lenard gives for a sulphide of similar composition $.377\,\mu$ and $.332\,\mu$ respectively, as shown in the upper diagram.

To obtain the absorption spectrum of these sulphides by transmission is impracticable on account of their great opacity, but the following procedure was in some instances successful. A thin layer of the substance was pressed between quartz plates, and mounted in front of the slit in such a position that rays from the spark would be diffusely reflected into the collimator of the spectrograph. Photographs which exhibited the selective absorption of the substance were thus obtained. The barium sulphide under investigation showed two narrow absorption bands, indicated below the base line in Fig. 1, and a region of general absorption beyond $.3\mu$. The two narrow bands whose crests as determined from the photographs were at $.375\mu$ and $.332\mu$ obviously correspond with the bands of excitation and sufficiently explain the existence of the latter.

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[8] V. Henri, *Physikalische Zeitschrift,* 14, p. 516, 1913.

[9] H. E. Howe, *Physical Review,* 2, VIII., December, 1916.

Similar coincidences between selective absorption and selective excitation were established in the case of the compound SrPbNaF at $.355\mu$ (Lenard's band $.358\mu$) and of SrZuF at $.360\mu$ and $.297\mu$ (Lenard's bands $.360\mu$ and $.297\mu$). The relation is therefore probably a general one, corresponding to that already demonstrated in the case of the selective action of infra-red rays upon phosphorescence of zinc sulphide, where the maximum effect was found in regions of maximum absorption.[10]

SPECTROPHOTOMETRIC MEASUREMENTS.

A detailed spectrophotometric study reveals widely varying degrees of complexity in the spectra of the different sulphides. Dr. H. L. Howes kindly made for the writer very careful measurements of three characteristic compounds, which may be regarded as preliminary to a more extended investigation.

His method, briefly stated, was as follows: The substance was mounted behind the disk of the synchrono-phosphoroscope and was illuminated by means of the radiation of the zinc spark; the disk being adjusted so as to afford observation of the phosphorescence in its earliest stages, *i. e.*, after a few ten thousandths of a second from the close of excitation. In place of the photometer used in taking curves of decay a spectrophotometer with two collimators, Lummer-Brodhun cube (L) and constant deviation prism was mounted as shown in Fig. 2. One collimator was directed towards the phosphorescent surface P, the other towards the comparison light A. The latter consisted of an acetylene flame properly screened. The two slits S, S of the spectrophotometer were of equal width and measurements were made by moving the flame along a photometer bar *B, B* in the prolonged axis of the collimator. Settings were made at intervals of 50 Ångström units throughout the spectrum. On account of the very great range of intensities within the phosphorescence spectrum it was necessary to increase the effective range of the photometer bar by the interposition of screens for which the reduction factors had been carefully determined.

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[10] Nichols and Merritt, "Studies in Luminescence," Publications of the Carnegie Institution, No. 152, p. 84.

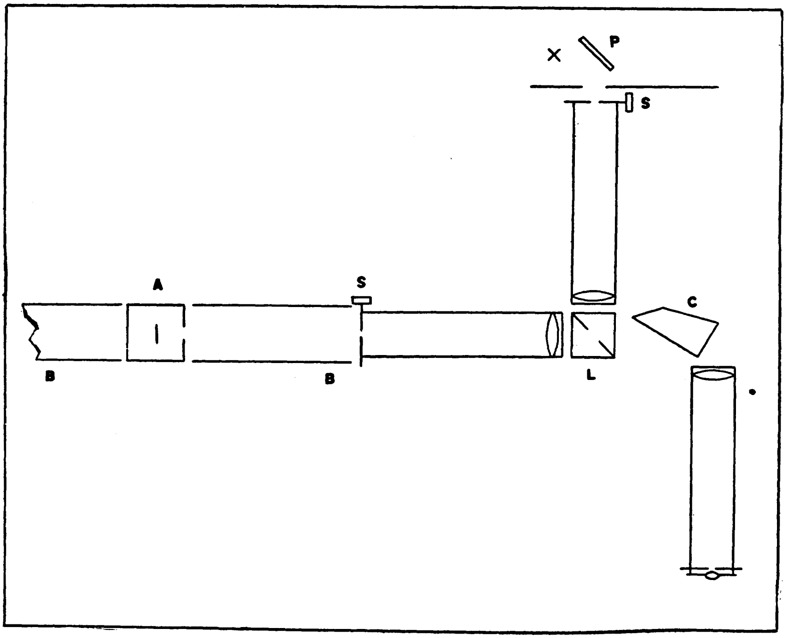

FIG. 2.

The first substance studied in this manner was a strontium sulphide, with bismuth as the active metal, designated as L. and K. No. 13. The spectrum curve obtained by Dr. Howes, using the method described above, is shown in Fig. 3. The complexity of the band is very obvious, there being subordinate crests on either side of the principal maximum.

The curve suggests at once a group of overlapping bands, so nearly merged that to the eye it would appear as a single simple band. There is moreover a distinct suggestion of a systematic relation.

Taking the relative frequencies, *i. e.,* reciprocals of the approximate wave-lengths ($1/\mu \times 10^3$), of the crests as estimated from the curve, it is found that the intervals are either very nearly 58 or twice that number. If a series having 58 as its constant interval be formed with one member located at the principal crest ($\lambda = 4800$) other members of this series will coincide with the subordinate crests of the curve. The short vertical lines in Fig. 3 indicate the positions of those members of such a series as coincide with the crests and of two further members which fall on a slight and not very well defined maxima at .5562 μ and .5921 μ.

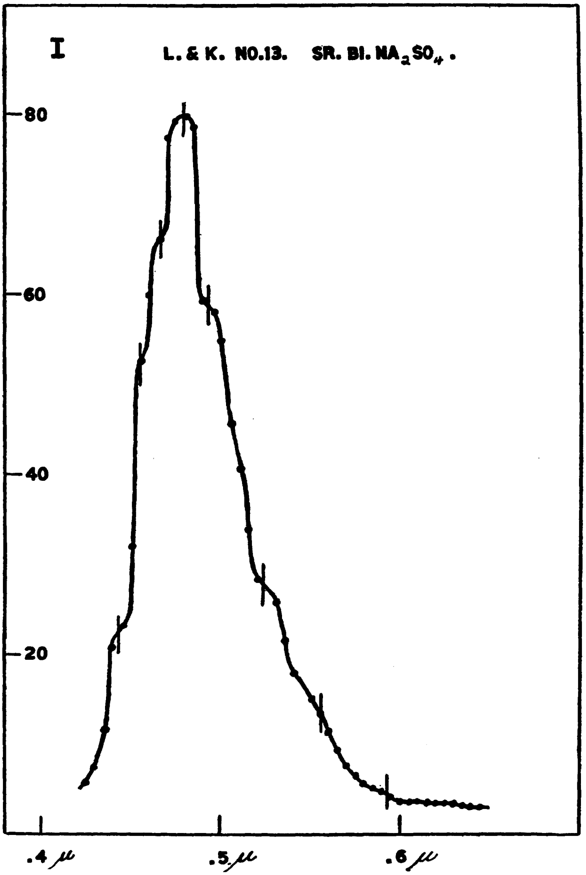

Fig. 3.

The agreement is sufficiently good throughout to warrant the statement that:

The band consists of a complex the overlapping components of which, so far as visible, are members of a series having a constant interval.

The following table gives the appproximate frequencies and wave-lengths.

TABLE I.

Approximate Frequencies and Wave-Lengths of Visible Crests in Spectrum of the Phosphorescent Sulphide L. and K. No. 13 (Sr. Bi, Na_2SO_4).

Visible Crests. μ	Series. $1/\mu \times 10^3$	Intervals.
.4430	2257	58
.4547	2199	58
.4670	2141	58
.4801	2083	58
.4938	2025	
——	1967	2 × 58
.5238	1909	
——	1851	2 × 58
.5562	1793	
——	1735	2 × 58
.5921	1677	

The three members of the above series not designated in the table as corresponding to visible crests have wave-lengths at .5084 μ, .5402 μ and .5764 μ and these fall upon less definite maxima on the curve than those which have been called *visible crests.*

Another substance investigated with the spectroscope was a calcium sulphide with bismuth as the active metal (L. and K. No. 3) which is notable for its intense blue phosphorescence.

The spectrum, as will be seen from Fig. 4, appears as a single crested band with a well-defined maximum of unusual brightness at about .447 μ. It is of the well-known typical form, steeper towards the violet and shows no visible evidence of complexity; but the phosphorescent light extends throughout the visible spectrum although of relatively very small intensity in the longer wave-lengths. Plotted to this scale no details of this weaker region can be seen but if the ordinates be increased one hundred fold, as in curve *BB,* various maxima and minima appear; indicating a second complex band, or overlapping group of bands which merge into the brilliant blue band at their more refrangible end.

This is in agreement with the fact recorded in a recent paper[11] that when this substance is excited to phosphorescence at the temperature of liquid air its color is blue-green instead of blue-violet on account of the suppression of the band of shorter wave-length which is dominant at ordinary temperatures.

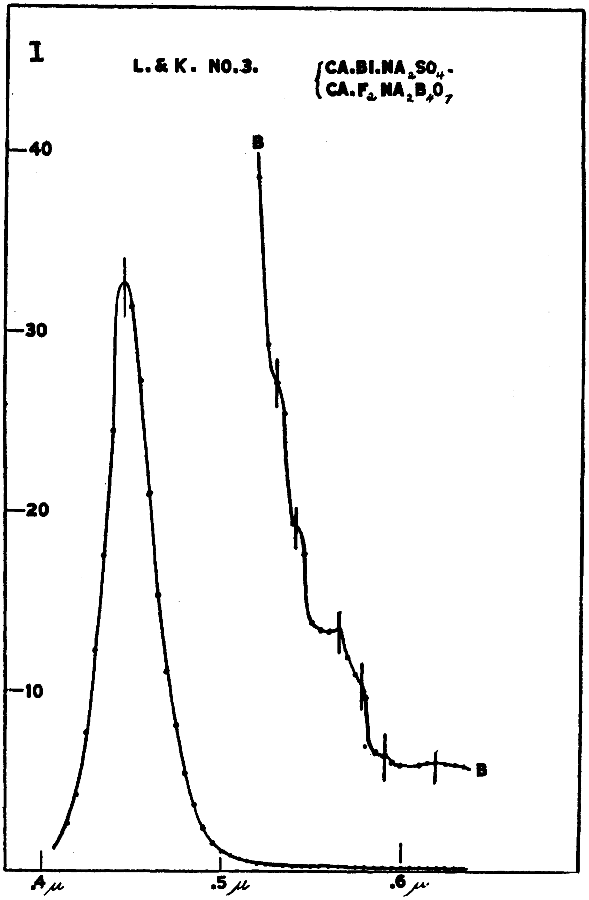

FIG. 4.

The crests shown in the curve *BB* also belong to a series of constant frequency interval, the approximate interval being 39. The location of the members of this series which coincide with maxima are indicated by vertical lines. Frequencies ($1/\mu \times 10^3$) and wave-lengths are given in Table II.

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[11] Nichols, PROC. OF THE AMERICAN PHILOS. SOCIETY, Vol. LV., p. 496, 1916.

TABLE II.

SERIES OF VISIBLE CRESTS IN THE SPECTRUM OF L. AND K. SULPHIDE NO. 3 (CaB_2').

Visible Crests. μ	Series. $1/\mu \times 10^3$	Interval from Series.
.5300	1887	39
.5411	1848	39
.5528	1809	39
.5650	1770	39
.5781	1731	39
.5910	1692	39
.6049	1653	39
.6200	1614	

Here every member of the series is represented by a recognizable, although in some cases somewhat indefinite maximum in the curve, as far as .5300 μ. If we extend the series further towards the violet we find that the ninth member beyond .5300 μ lies at .4468 μ (frequency 2238) and this coincides with the main crest well within the errors of observation. There are other barely discernible indications of submerged crests on either side of the principal crest.

The most striking example investigated in this preliminary study is that presented by L. and K. No. 33, a barium sulphide with copper.

Here we have obviously two overlapping complexes of bands (see Fig. 5), at least 14 crests of which are indicated more or less definitely by the irregularities in the spectrum curve.

In this case the bands fall into two groups. From wave-length .5 μ towards the violet the frequency intervals between neighboring crests are all multiples of 70. Towards the red the interval is 26.6 for all but one band. This band at .5376 μ falls however into the series having the constant interval of 70.

To indicate the closeness of the agreement vertical lines have been drawn on the diagram in Fig. 5, as in the previous cases, at wave-lengths corresponding to those members of the two series of constant interval which coincide with observable crests. Solid lines belong to the group with an interval 70, dotted lines to the 26.6 interval. Wave-lengths, reciprocals and intervals are given in Table III.

The designation of these series as of constant interval, upon the basis of the curves in Figs. 3, 4 and 5, can be tentative and approximate only; but no systematic departure large enough to be detected appears to exist. The wave-lengths given in the tables are those of the vertical lines and therefore of the members of the constant interval series which coincide with the various crests. No independent

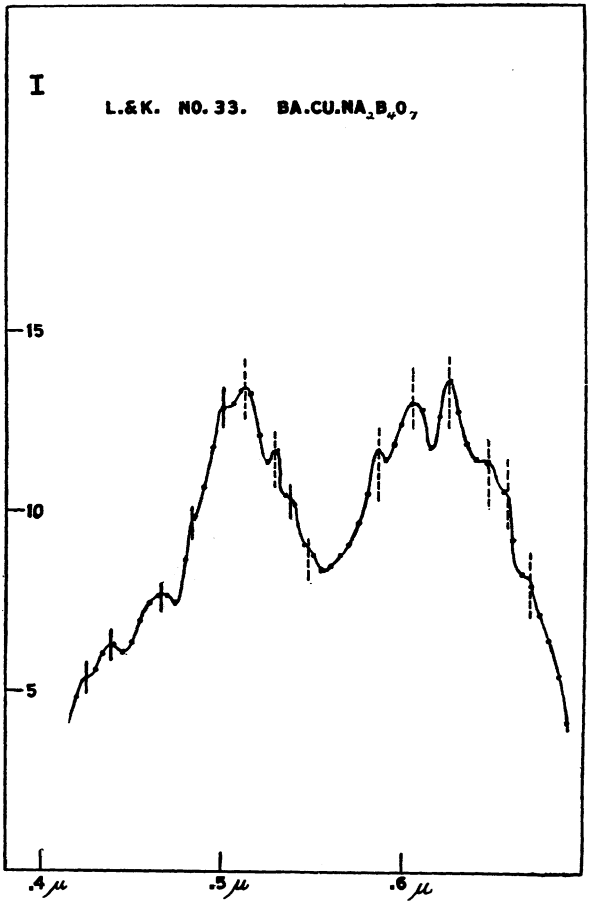

FIG. 5.

estimates of the wave-lengths would seem to be significant. The curves however were plotted directly from the spectrophotometric readings without reference to any possibly symmetrical arrangement of the crests.

TABLE III.

Approximate Frequencies and Wave-Lengths of Visible Crests in the Spectrum of the Phosphorescent Sulphide L. and K. No. 33.

Visible crests with interval = 70.

Wave-Lengths.	Frequencies $1/\lambda \times 10^3$.	Intervals.
4255	2350	70
4386	2280	
——		70 × 2
4673	2140	70
4831	2070	70
5000	2000	
——		70 × 2
5376	1860	

Visible crests with interval = 26.6.

Wave-Lengths.	Frequencies.	Intervals.
5000 μ	2000.0	26.6 × 2
5136	1946.8	26.6 × 2
5283	1892.6	26.6 × 7
5861	1706.4	26.6 × 2
6049	1653.2	26.6 × 2
6250	1600.0	26.6 × 2
6465	1546.8	
6578	1520.2	26.6
6695	1493.6	26.6

Whether the spectra under consideration are to be regarded as consisting of a single band or of more than one band is not a question of complexity of structure. Any system, however complex, which behaves as a unit under varying conditions of temperature, mode of excitation, etc., all the components being affected in like manner, may be considered as a single band in the sense in which that term has been used by Lenard. We have a striking example indeed of such bands or systems of great complexity of structure in the case of the uranyl salts.

The evidence that, in general, the spectra of the phosphorescent sulphides contain more than one band or complex has already been mentioned, *e. g.*, the marked changes of the color of phosphorescence with temperature and during the process of decay, the change of color with the mode of excitation as described by Becquerel, etc.

In the three sulphides the spectra of which have just been discussed it was thought probable that in spite of the overlapping of the components something might be learned by observing the decay of phosphorescence of different regions of the spectra separately and for this purpose Drs. Howes and Hodge made the following determinations.

THE DECAY OF PHOSPHORESCENCE IN DIFFERENT PORTIONS OF THE SPECTRUM.

To obtain the curve of decay for a restricted region of the spectrum the spectrophotometer was used in combination with the synchrono-phosphoroscope and photometer bar as described in a previous paragraph (see Fig. 2). The collimator slits which, to secure the greatest possible detail in the spectrophotometric measurements had been very narrow, were opened to a width of 2.0 mm. so that the brightness of the contrast field would be sufficient to allow the observer to follow the rapidly fading phosphorescence even in the weaker portions of the spectrum.

The spectrophotometer was set for a selected region and the curve of decay was obtained in the usual manner by observing the position of the comparison lamp upon the photometer bar which gave equality in the contrast field for increasing times after the close of excitation. The range of the readings was from .001 sec. to .03 sec. according to the position of the sectored disk upon the shaft of the phosphoroscope.

In this way a set of curves corresponding to several nearly equidistant regions within the phosphorescence spectrum was obtained for each of the three sulphides under consideration.

Three such curves for the Ca, Bi sulphide No. 3, plotted with $I^{-1/2}$ as ordinates, are shown in Fig. 6; four for the Sr, Pb sulphide No. 13 in Fig. 7 and three for the Ba, Cu sulphide No. 33 in Fig. 8. A notable feature of all these curves is the existence of two so-called linear processes the first of steeper slope and therefore indicative of a more rapid decay of phosphorescence than the second. This form of curve, as is well known, is characteristic of phosphorescent substances in general, the only well established exceptions being those occurring in the case of the uranyl salts.[12] As regards the relation of the two processes recorded in these diagrams to what appear as the first and second processes in the usual study of the long time phosphorescence of such sulphides, it is clear that the second process

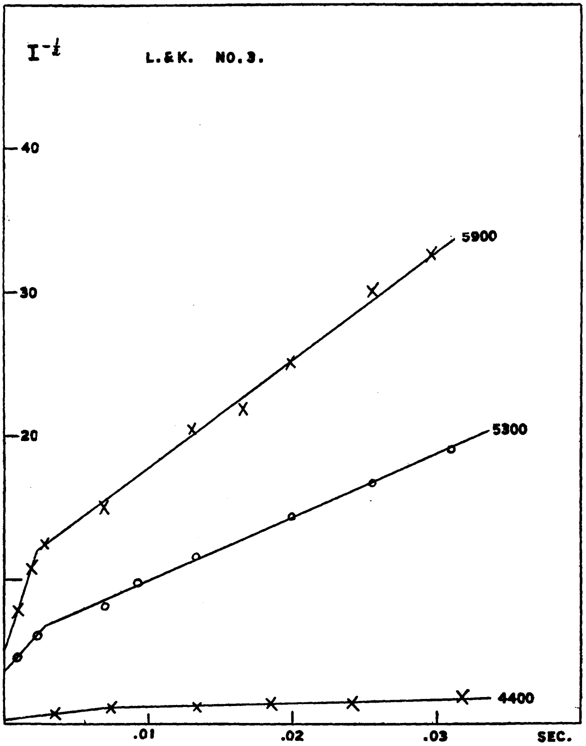

Fig. 6.

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[12] Nichols, *Proc. Nat. Academy of Sciences,* II., p. 328, 1916.

in our curves is not identical with the first process as observed by the usual long time methods.

Assuming the second process to continue; the intensity after 1 second would be about 1/1,000 of that at .01 sec. or roughly 1/20,000 of its initial brightness; whereas as is well known these substances retain an easily visible phosphorescence after many seconds.

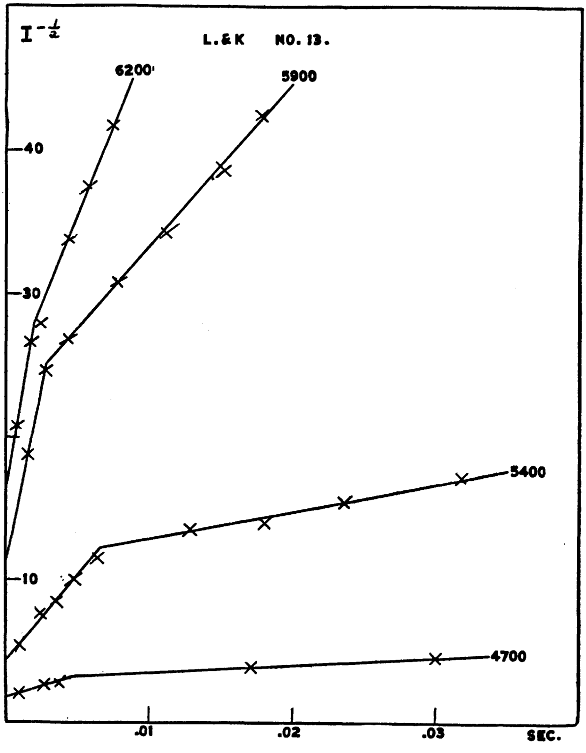

FIG. 7.

This can only be accounted for by supposing that one or more later processes of successively slower decay follow one another; making up a more complicated curve of decay than has generally been assumed. Carl Zeller,[13] the only previous investigator to determine the earlier stage of this type of phosphorescence, has published a diagram which overlaps the range of the present experiments. Three of his curves are for a Sr, Bi; Ca, Bi and Ba, Cu sulphide respectively; corresponding to and possibly identical with our 13, 3 and 33. These show a linear process which he regards as the first process in the decay and which, as he points out, has, in each case, a much steeper slope than the first process, so called, obtained by observations covering the range from a second or more onwards. The slope of his lines considering the range from .01^s to .03^s and remembering that Zeller did not determine the decay for various regions of the spectrum separately are fairly comparable with the second process (beyond the knee) in Figs. 6 and 7 if we select the regions including the principal crest. We may therefore regard Zeller's process which extends as far as .06 second as the same as our second process.

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[13] Zeller, *Physical Review*, (1), 31, p. 367; also Carnegie Publications, No. 152, p. 124.

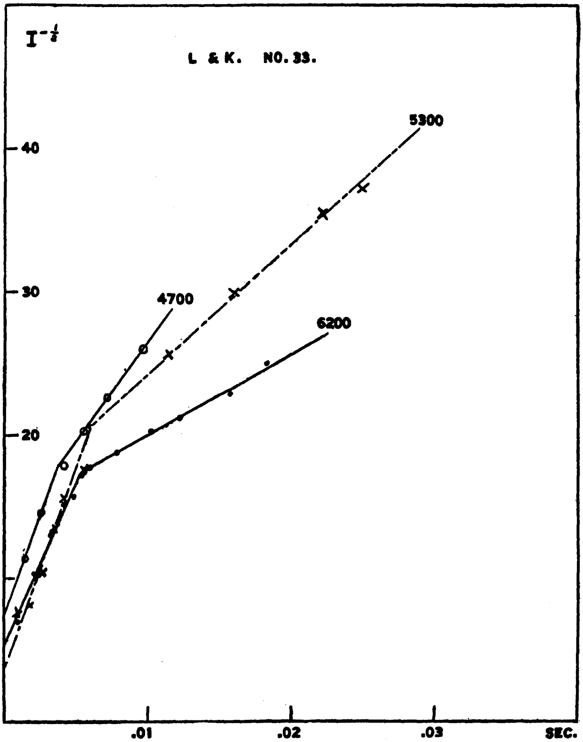

Fig. 8.

The change of slope between this process and the *first process* so called in the curves of decay for these sulphides as observed during the interval from two seconds onward is very great. In a representative curve obtained by Mr. Carleton E. Power[14] for example his first process extends for nearly 50 seconds. The slope if computed for a time scale such as that used in our measurements where 1/100 sec. may be taken as a convenient unit, is scarcely perceptible. The increase in the ordinate ($I^{-1/2}$) in passing from time .01 sec. to .02 sec. in our second process or in Zeller's process is of the order

$$\frac{I_{02}^{-1/2}}{I_{01}^{-1/2}} = 1.2;$$

Power's first process would give a ratio of the order of 1.008.

In other words during the first few hundredths of a second after the close of excitation the intensity of phosphorescence falls in each 1/100 of a second from unity to about .70 while after several seconds, it falls in 1/100 second only from unity to .99.

It seems probable, assuming continuity in the progress of the decay, that if we had a complete curve of decay for one of these sulphides, the knee between our second process and the first process of the long-time curves would be found to lie somewhere between 0.10 second and 1.0 second. If it occurs much earlier than 0.10 second, Zeller would have discovered it; if much beyond 1.0 second it should appear in the long-time measurements. In fact many curves for the decay of phosphorescence by the latter process do show a downward trend and Lenard, among others, has disputed the linear character of the curve as we approach the origin of time. The existence of at least four linear processes each of longer duration and lesser slope than the preceding may well account for the difference of opinion. An observer determining the law of decay as a whole by a method not taking cognizance of time intervals of less than say 1/10 second, would describe as a curve what under much more detailed study might be revealed as a succession of linear processes.

Owing to the overlapping of the components in the spectra under consideration it is difficult to determine whether the group of equidistant bands are to be regarded as a unit, as in the case of the uranyl salts, or indeed whether they constitute the whole of the phosphorescence spectrum. To that end some method permitting of more complete resolution must be devised. The pronounced changes in the color of the phosphorescent light would make it seem probable that we have to do in these observations chiefly with components of the phosphorescence that are of rapid decay and which, after a few hundredths of a second, disappear leaving behind other components which constitute the phosphorescence of long duration. These, which are probably of relatively insignificant initial brightness, doubtless overlap the phosphorescence of short duration but occupy, as a whole, a somewhat different portion of the spectrum.

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[14] Power, C. E., Manuscript Thesis in the Library of Cornell University.

In that case since one has to do with a different group of bands in observing the initial and the later phases of phosphorescence there would be an actual discontinuity between the processes discussed above and the great change of slope is readily explained.

SUMMARY.

1. The regions of selective excitation (the bands of excitation for the Lenard and Klatt sulphides, are shown to coincide in position and extent with absorption bands in the transmission spectrum.

2. The spectrum of the phosphorescent light, during the first few thousandths of a second after the close of excitation, contains one or more groups of overlapping bands, the crests of each group forming a spectral series having a constant frequency interval.

3. The decay of phosphorescence during the first three hundredths of a second after the close of excitation may be described as consisting of two processes each showing a linear relation between $I^{-1/2}$ and time. The first and more rapid process lasts for less than .01 second for the three sulphides studied under the intensity of excitation employed. The second process probably persists for .06 second or more.

4. The phosphorescence of long duration of the sulphides under consideration is probably due to another group of bands of comparatively feeble initial brightness which come under observation only after the phosphorescence of short duration has vanished.

CORNELL UNIVERSITY,
DEPARTMENT OF PHYSICS,
March, 1917.